PHYSICAL REVIEW LETTERS

Onsager-Manning-Oosawa Condensation Phenomenon and the Effect of Salt

Emmanuel Trizac

Theoretical Biological Physics, UCSD, La Jolla, California 92093, USA,
and Physique Théorique et Modèles Statistiques, Université Paris-Sud, UMR CNRS 8626, Bâtiment 100, 91405 Orsay Cedex, France

Gabriel Téllez

Departamento de Física, Universidad de Los Andes, Apartado Aéreo 4976, Bogotá, Colombia

Making use of results pertaining to Painlevé III type equations, we revisit the celebrated Onsager-Manning-Oosawa condensation phenomenon for charged stiff linear polymers, in the mean-field approximation with salt. We obtain analytically the associated critical line charge density and show that it is severely affected by finite salt effects, whereas previous results focused on the no salt limit. In addition, we obtain explicit expressions for the condensate thickness and the electric potential. The case of asymmetric electrolytes is also briefly addressed.

PACS numbers: 82.35.Rs, 61.20.−p, 87.15.−v

Whereas scaling approaches have proven useful to describe neutral polymers, our understanding of polyelectrolytes solutions is quite rudimentary, due to the long range character of Coulombic interactions [1,2]. Stiff linear polyelectrolytes that are free of the coupling between chain conformation and small ions degrees of freedom consequently provide ideal systems for a comprehensive comparison between theory and experiments. There indeed exists a large variety of such rodlike polyions, ranging from synthetic polymers [e.g., those based on poly(p-phenylene) backbones [3]] to biological molecules (DNA, actin filaments, microtubules, some viruses, etc.). On distances smaller than their (large) persistence length, these objects behave as charged cylinders with an associated logarithmic electrostatic potential that may be strong enough to bind oppositely charged microions (counterions). This was first realized by Onsager and analyzed by Manning [4] and Oosawa [5]: in the limit of vanishing polymer radius, the corresponding phenomenon of counterion condensation is triggered when the so-called Manning parameter $\xi = \ell_B/\ell$ is larger than unity [1,2]. Here, ℓ^{-1} is the backbone line charge in units of the elementary charge e and $\ell_B = e^2/(\epsilon kT)$ denotes the Bjerrum length with ϵ the dielectric constant of the solvent and kT the thermal energy.

Counterion condensation, which affects a gamut of static and dynamical properties, is central to our view of highly charged polymers and an active field of research [6–11]. Interestingly, the influential arguments of Onsager, Manning, and Oosawa found confirmation and a firm basis in numerical and analytical studies of the mean-field nonlinear Poisson-Boltzmann (PB) equation where the densities of microions with valency z are related to the local mean electrostatic potential φ by $n_z \propto \exp(-ze\varphi/kT)$. The basic features are already present in the exact solution of PB theory for a charged cylinder in a concentric cylindrical Wigner-Seitz cell without salt [12], which can be cast as a restricted version of a partial differential equation

first studied and solved by Liouville in 1853 [13], as pointed out in [14]. For an isolated cylinder (i.e., in the limit of a diverging Wigner-Seitz cell radius) with a small charge $\xi < 1$, no counterions are bound to the cylinder and the potential distribution reduces to the bare logarithmic form. On the other hand, for $\xi > 1$, a finite fraction of ions are ''bound'' to the surface [15].

The physically relevant situation where salt is present (i.e., with both co- and counterions, which may come from the dissociation of an added electrolyte and/or from the solvent itself) has resisted analytical understanding much longer. Ramanathan showed that for $\xi > 1$ and distances much larger than the polyion radius a the ionic atmosphere was the same as that due to a cylinder with charge parameter $\xi = 1$ [16]. This result holds asymptotically for $\kappa a \to 0$ [16,17], where κ^{-1} is the Debye length [1,2]. This condensation effect is the counterpart of the aforementioned one and was placed within the mathematical framework of isomonodromy theory in Ref. [18] and Painlevé III equations in Refs. [18–20]. This drew an exact correspondence with Ising model correlators but more importantly allowed one (a) to compute the exact far-field behavior [18], (b) to show rigorously the critical nature of the value $\xi = 1$ when $\kappa a \to 0$ [6,18], and (c) to obtain some analytical results for the potential distribution and ionic densities [8]. The common framework to the previous approaches is PB theory, to which we will restrict ourselves in the subsequent analysis. Most of existing results hold for $\kappa a \to 0$ only, and it appears that this (singular) limit is approached logarithmically slowly. From a practical point of view, finite κa corrections can therefore never be discarded.

The purpose of the present work is to analyze the fate of the counterion condensation phenomenon at finite salt concentration ($\kappa a \neq 0$). We shall show that for $\kappa a < 1$ the transition is smoothed but remains, and that the associated critical charge parameter is salt dependent and smaller than the usual Manning threshold $\xi_c = 1$. The condensate structure will be resolved without the need to

invoke any matching procedure, and analytically tractable results will be obtained for the electric potential below and above the critical value ξ_c. Extensive use will be made of results pertaining to the theory of Painlevé III equations [20], which mathematical difficulty has—to the best of our knowledge—prevented to find a way towards the physicists' community [21]. The case of asymmetric 1:2 and 2:1 electrolytes—that are physically not equivalent [22]—will also be briefly addressed. Most of our results hold for $\kappa a < 1$ and by comparison with numerical results can be shown to be very accurate in this parameter range.

We consider Poisson's equation in cylindrical coordinates for the dimensionless electric potential (ϕ):

$$\frac{d^2\phi}{dr^2} + \frac{1}{r}\frac{d\phi}{dr} = -\frac{\kappa^2}{z_+ - z_-}[e^{-z_+\phi} - e^{-z_-\phi}], \quad (1)$$

for the situations $(z_+, z_-) = (1, -1)$, $(1, -2)$, or $(2, -1)$, other asymmetries unfortunately resisting the analysis. We demand that $rd\phi/dr = -2\xi$ for $r = a$ where the dimensionless bare charge of the polyion, ξ, is assumed positive without loss of generality. The second boundary condition ($\phi \to 0$ when $r \to \infty$) ensures that, at large distances, ϕ obeys the linearized equation $\nabla^2\phi = \kappa^2\phi$ and therefore takes the form

$$\phi(r) \underset{r\to\infty}{\sim} \frac{2\xi_{\text{eff}}}{\kappa a K_1(\kappa a)} K_0(\kappa r), \quad (2)$$

where K_0 and K_1 denote the modified Bessel functions of the second kind, of order 0 and 1, respectively. The prefactor defining the *a priori* unknown effective charge ξ_{eff} reduces by definition to the bare charge ξ for low values of ξ (linear regime) but nonlinear effects significantly affect ξ_{eff}. In particular, a consequence of counterion condensation is that for $\kappa a \to 0$ the former quantity no longer depends on ξ provided $\xi > 1$ [6,16,18]. We first focus on 1:1 electrolytes for which the electric potential ϕ_{11} crucially depends on a parameter λ [18,20] that in the present context is related to the effective charge through

$$\xi_{\text{eff}} = 2\kappa a K_1(\kappa a)\lambda \quad (3)$$

so that at large distances $\phi \sim 4\lambda K_0(\kappa r)$. For $\lambda < 1/\pi$ (which corresponds to $\xi < \xi_c$, where ξ_c is a critical charge to be defined below), Theorem 3 of Ref. [20] implies the short distance behavior

$$e^{-\phi_{11}/2} = (\kappa r)^\sigma B\left[1 - \frac{(\kappa r)^{2-2\sigma}}{16B^2(1-\sigma)^2}\right] + \mathcal{O}(\kappa r)^2, \quad (4)$$

where

$$B = 2^{-3\sigma}\frac{\Gamma[(1-\sigma)/2]}{\Gamma[(1+\sigma)/2]}, \quad (5)$$

Γ being the Euler function. On the other hand, for $\lambda > 1/\pi$, there is a qualitative change of behavior for ϕ_{11}:

$$e^{-\phi_{11}/2} = \frac{\kappa r}{4\mu}\sin\left[2\mu\log\left(\frac{\kappa r}{8}\right) - 2\Psi(\mu)\right] + \mathcal{O}(\kappa r)^4, \quad (6)$$

where Ψ denotes the argument of $\Gamma(i\mu)$ [20]. For our purposes, a very accurate approximation—considered in the remainder—is given by the small μ Taylor expansion $\Psi(\mu) \simeq -\pi/2 - \gamma\mu$, with $\gamma \simeq 0.5772\ldots$ the Euler constant. Both quantities σ (defined only for $\lambda < 1/\pi$) and μ (defined only for $\lambda > 1/\pi$) are positive and related to the bare charge by the boundary condition $r\phi'(r) = -2\xi$ at $r = a$: expressions (4) and (6) yield

$$\xi = \sigma - \frac{(2-2\sigma)(\kappa a)^{2-2\sigma}}{16(1-\sigma)^2 B^2 - (\kappa a)^{2-2\sigma}}, \quad (7)$$

$$(\xi - 1)\tan[2\mu\log(\kappa a/8) + 2\mu\gamma] = 2\mu, \quad (8)$$

where it is understood that μ is the smallest positive root of (8). As such, σ and μ characterize the short distance features, and the difficulty amounts to connecting these parameters with the far-field quantity λ. It may be shown that [18,20]

$$\lambda = \frac{1}{\pi}\sin\left(\frac{\pi\sigma}{2}\right) \quad \text{for } \lambda < \pi^{-1} \text{ (or } \xi < \xi_c), \quad (9)$$

$$\lambda = \frac{1}{\pi}\cosh(\pi\mu) \quad \text{for } \lambda > \pi^{-1} \text{ (or } \xi > \xi_c). \quad (10)$$

The leading order term in ϕ_{11} is therefore $-2\sigma\log(\kappa r)$ for $\lambda < \pi^{-1}$, which corresponds to the bare potential of a cylinder with line charge σ. For $\lambda > \pi^{-1}$ the dominant small r behavior reads $-2\log(\kappa r)$, up to an r-independent term varying with charge and salt content [23].

The change of behavior displayed by Eqs. (4) and (6) is the fingerprint of counterion condensation. The exponent σ fulfills $0 \leq \sigma \leq 1$, and for the critical value $\lambda = 1/\pi$, we have $\sigma = 1$ while μ vanishes. The corresponding critical value of ξ either follows from (4) taking the limit $\sigma \to 1^-$ or enforcing $\mu \to 0^+$ in Eq. (6). These two routes yield exactly the same critical charge:

$$\xi_c = 1 + \frac{1}{\log(\kappa a) + \gamma - \log 8}. \quad (11)$$

In the limit $\kappa a \to 0$, the celebrated Manning threshold $\xi_c = 1$ is recovered but the correction embedded in (11) is significant: at $\kappa a = 10^{-3}$, ξ_c is shifted to 0.881, and at $\kappa a = 0.1$, we get $\xi_c \simeq 0.737$. Expression (11) has been derived omitting corrections of order $(\kappa r)^2$ in (4) and of order $(\kappa r)^4$ in (6). One may show, however, that the next correction to (11) is of order $(\kappa a)^4(\log\kappa a)^2$, and is therefore irrelevant from a practical point of view whenever $\kappa a < 1$ [24]. Figure 1 may be considered as illustrating a "law of corresponding states" and shows the values of bare charge and salt concentration (or equivalently polyion radius) leading to the same electrostatic potential: if σ or μ is fixed, the connection formulas (9) and (10) indeed ensure that λ is also fixed, so that moving along the contour lines of Fig. 1 leaves the full function $\phi(\kappa r)$ unaffected. The complementary information of the ξ dependence of σ and μ at fixed salt concentration is shown in Fig. 2. It appears that, except in the vicinity of ξ_c, σ is very close to
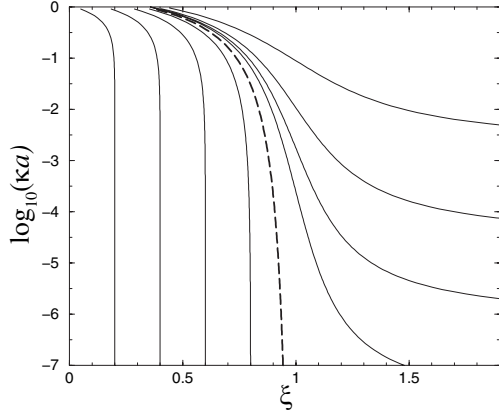
FIG. 1.   Contour lines for σ and μ (and hence for λ) in the charge-salt plane, as deduced from Eqs. (7) and (8). The thick dashed curve shows the locus of critical charges ξ_c and separates the iso-σ curves for $\xi < \xi_c$ (from left to right, the curves correspond to $\sigma = 0.2, 0.4, 0.6,$ and 0.8) from the iso-μ curves shown—on the right-hand side—for $\xi > \xi_c$ (from bottom to top, $\mu = 0.08, 0.1, 0.13,$ and 0.2).

ξ (with systematically $\sigma > \xi$). Close to the transition threshold, one has $\sigma - 1$ and μ scaling as $|\xi - \xi_c|^{1/2}$. For highly charged polyions, the argument of the tangent function in (8) has to be close to $-\pi$, from which we obtain

$$\mu \simeq \frac{-\pi/2}{\log(\kappa a) + \gamma - \log 8 - (\xi - 1)^{-1}}. \qquad (12)$$

The inset of Fig. 2 assesses the quality of this approximation, which improves when ξ increases but fails quite severely when $\xi < 1 + \mathcal{O}(1/\log \kappa a)$.

We have tested the accuracy of expressions (4), (7), and (9) below the critical charge, and Eqs. (6), (8), and (10) for $\xi > \xi_c$ against numerical solutions of the full nonlinear PB
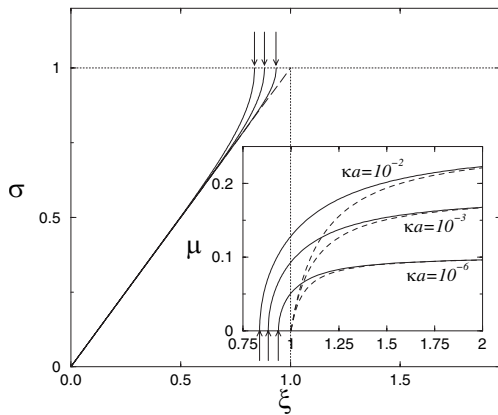

FIG. 2. σ versus bare charge. In the main graph and in the inset, three values of κa have been chosen. From left to right, $\kappa a = 10^{-2}, 10^{-3},$ and 10^{-6}. For $\kappa a \to 0$, $\sigma \to \xi$ (see the dashed first bisectrix) while $\mu \to 0$. The associated critical charges are indicated by the arrows (also in the inset). The inset shows μ versus ξ, and the dashed curves correspond to approximation (12). The vertical line indicates $\xi = 1$.

Eq. (1). These formulas turn out exceptionally accurate for small r, while the far field is conversely equally well given by (2) where ξ_{eff} is determined by (3). More interestingly, for $\kappa r < 1/2$, ϕ_{11} deduced from (4) is extremely accurate for all possible charges and $\kappa a < 0.1$ (curves not shown). Similarly, the far-field expression (2) provides very good accuracy as soon as $\kappa r > 1/2$. It therefore appears that ϕ_{11} is analytically known at all distances; in the crossover region $\kappa r \simeq 0.5$, where no limiting expression is supposed to be reliable, the worst relative accuracy is observed but is nevertheless always below 2%. We emphasize here that ξ_{eff} significantly differs from the critical charge ξ_c. In other words, even treating correctly the condensation phenomenon, nonlinear effects are still present and affect the diffuse cloud of remaining "uncondensed" ions that cannot be treated within linearized PB or Debye-Hückel theory. This important aspect has been overlooked so far (see, e.g., [4]) and is present even in the simplest limit $\kappa a \to 0$, where $\xi_{\text{eff}} \to 2/\pi$ irrespective of ξ (provided $\xi > \xi_c$), whereas $\xi_c = 1$. The resulting repulsive force of interaction between two highly charged rods is therefore overestimated by a factor $\mathcal{F} = (\pi/2)^2 \simeq 2.5$ in the traditional Manning-Oosawa picture. An experimental check of this prediction has to fulfill the requirement of very low salt, since at, say, $\kappa a = 10^{-2}$, $\mathcal{F} \simeq 1.4$; see Eq. (3).

The previous results allow one to discuss in a rigorous manner several aspects of polyelectrolyte physics investigated in the literature. Of particular interest is the so-called Manning radius R_M [9,10], introduced to quantify the condensate thickness when $\xi > \xi_c$. In the Wigner-Seitz cell approach, the integrated line charge $q(r) = -r\phi'(r)/2$ has an inflexion point when plotted as a function of $\log r$ at the distance R_M where $q(R_M) = 1$ [9,25]. It is remarkable that the $q(r)$ following from (6) shows the very same feature, which is ascribable to a similar functional form, although at finite salt concentration $q(a) \equiv \xi = 1$ no longer provides the critical value of the charge. The corresponding Manning radius reads

$$\kappa R_M = 8 \exp[-\pi/(4\mu) - \gamma]. \qquad (13)$$

When $\xi > 1 + \mathcal{O}(1/\log \kappa a)$, one may use the approximation (12) and therefore

$$\kappa R_M \simeq 2\sqrt{2\kappa a} \exp\left(-\frac{\gamma}{2} - \frac{1}{2(\xi - 1)}\right). \qquad (14)$$

The latter formula is the central result of a recent work [10] where it was obtained by a clever but approximate matching procedure. It appears to be incorrect when μ deviates from the large ξ expansion (12) (see the inset of Fig. 2 where it is seen that the difference between the dashed and continuous curves may be large). On the other hand, Eq. (13) is always found to be very accurate compared to the numerical solutions of PB equation [24]. We note that choosing a different definition for the condensate thickness R^* [e.g., demanding that $q(R^*) = \xi_c$ instead of unity] leads for large bare charges to the scaling relation $R^* \propto a^\alpha \kappa^{\alpha-1}$

with now $\alpha = (\arctan \pi)/\pi \simeq 0.402$, smaller than the value $\alpha = 1/2$ appearing in (14). The convenient inflection point criterion alluded to earlier would, however, be lost following such a route.

We now turn to the case of asymmetric 1:2 and 2:1 electrolytes [22]. Recent results obtained for a class of solutions to the cylindrical Toda equations [26] allow one to extend the above analysis to such situations. So far, the 1:2 case only has been studied, again only in the limit $\kappa a \to 0$ [8]. The details will be provided elsewhere [24]; we concentrate here on the critical charges

$$\xi_c^{1:2} = \frac{1}{2} + \frac{1}{2\log(\kappa a) + 2C^{1:2}}, \qquad (15)$$

$$\xi_c^{2:1} = 1 + \frac{1}{\log(\kappa a) + C^{2:1}}, \qquad (16)$$

with

$$C^{1:2} = \gamma - (\log 2)/3 - 3(\log 3)/2 \simeq -1.301, \qquad (17)$$

$$C^{2:1} = \gamma - \log 2 - 3(\log 3)/2 \simeq -1.763. \qquad (18)$$

The associated Manning radii, defined from $q(R_M) = 1$ (2:1 case) or $q(R_M) = 1/2$ (1:2 case)—which again ensures the existence of an inflection point criterion—read

$$\kappa R_M^{1:2} \simeq 2^{-1/3} 3^{3/4} \sqrt{2\kappa a} \exp\left[-\frac{\gamma}{2} - \frac{1}{2(2\xi - 1)}\right], \qquad (19)$$

$$\kappa R_M^{2:1} \simeq 3^{3/4} \sqrt{2\kappa a} \exp\left[-\frac{\gamma}{2} - \frac{1}{2(\xi - 1)}\right]. \qquad (20)$$

These expressions have the same status as (14), i.e., hold at high enough ξ. It appears that the Manning 2:1 radius is inflated a factor $3^{3/4}/2 \simeq 1.14$ compared to its 1:1 counterpart, irrespective of salt content and charge (but beyond the condensation threshold). This quantifies the intuitive picture of a swollen double layer due to the presence of divalent coions (expelled further away than monovalent ones), and conversely of a shrunk cloud (by a factor $2^{-4/3} 3^{3/4} \simeq 0.90$ when ξ is large enough) in the 1:2 case due to the more efficient screening.

To conclude, exploiting an important body of mathematical work in the field of stiff polyelectrolytes allows one to systematically address finite salt effects that are crucial even under experimentally low salt conditions. The present work sheds new light on the condensate structure and further connects short scale features with the long range behavior of the electric potential. Among the consequences of experimental relevance following from our analysis, we mention the large k behavior of the counterion/rod S_- and coion/rod S_+ partial structure factors, expected to scale as $k^{-2 \pm 2\sigma}$ for $\xi < \xi_c$, with $S_- \underset{k \to \infty}{\propto} 1/\log k$ at $\xi = \xi_c$. Such effects are missed following the classical Manning-Oosawa arguments, which generally result in an underestimation of screening.

[1] J.-L. Barrat and J.-F. Joanny, Adv. Chem. Phys. **94**, 1 (1996).
[2] Y. Levin, Rep. Prog. Phys. **65**, 1577 (2002).
[3] C. Holm, M. Rehahn, W. Oppermann, and M. Ballauff, Adv. Polym. Sci. **166**, 1 (2004).
[4] G. S. Manning, J. Chem. Phys. **51**, 924 (1969); **51**, 934 (1969).
[5] F. Oosawa, *Polyelectrolytes* (Dekker, New York, 1971).
[6] A. L. Kholodenko and A. L. Beyerlein, Phys. Rev. Lett. **74**, 4679 (1995).
[7] I. Rouzina and V. A. Bloomfield, Biophys. Chem. **64**, 139 (1997); Y. Levin and M. Barbosa, J. Phys. II (France) **7**, 37 (1997); A. Deshkovski, S. Obukhov, and M. Rubinstein, Phys. Rev. Lett. **86**, 2341 (2001); P. L. Hansen, R. Podgornik, and V. A. Parsegian, Phys. Rev. E **64**, 021907 (2001); M. L. Henle, C. D. Santangello, D. M. Patel, and P. A. Pincus, Europhys. Lett. **66**, 284 (2004); M. Muthukumar, J. Chem. Phys. **120**, 9343 (2004).
[8] C. A. Tracy and H. Widom, Physica (Amsterdam) **244A**, 402 (1997).
[9] M. Deserno, C. Holm, and S. May, Macromolecules **33**, 199 (2000).
[10] B. O'Shaughnessy and Q. Yang, Phys. Rev. Lett. **94**, 048302 (2005).
[11] A. Naji and R. R. Netz, Phys. Rev. Lett. **95**, 185703 (2005).
[12] T. Alfrey, Jr., P. W. Berg, and H. Morawetz, J. Polym. Sci. **7**, 543 (1951); R. M. Fuoss, A. Katchalsky, and S. Lifson, Proc. Natl. Acad. Sci. U.S.A. **37**, 579 (1951).
[13] J. Liouville, J. Math. Pures Appl. **18**, 71 (1853).
[14] A. Fogden, J. Daicic, D. J. Mitchell, and B. W. Ninham, Physica (Amsterdam) **234A**, 167 (1996).
[15] For a clear summary, see, e.g., Appendix A of R. R. Netz and J.-F. Joanny, Macromolecules **31**, 5123 (1998).
[16] G. V. Ramanathan, J. Chem. Phys. **78**, 3223 (1983).
[17] M. Fixman, J. Chem. Phys. **70**, 4995 (1979).
[18] J. S. McCaskill and E. D. Fackerell, J. Chem. Soc., Faraday Trans. 2 **84**, 161 (1988).
[19] See, e.g., H. T. Davis, *Introduction to Nonlinear Differential and Integral Equations* (Dover, New York, 1962).
[20] B. M. McCoy, C. A. Tracy, and T. T. Wu, J. Math. Phys. (N.Y.) **18**, 1058 (1977).
[21] PB theory may be cast into a Painlevé III problem for cylindrical polyions only [18]. Consequently, much less analytical results exist for charged spheres.
[22] In the 1:2 (2:1) situation, coions are monovalent (divalent) while counterions are divalent (monovalent).
[23] We emphasize, however, that subleading corrections embodied in Eqs. (4) and (6) are always relevant when numerical accuracy is pursued.
[24] G. Téllez and E. Trizac (to be published).
[25] The inflection point criterion may be extended beyond mean field; see [9].
[26] C. A. Tracy and H. Widom, Commun. Math. Phys. **190**, 697 (1998).